Growth of ZnO Nanorods in Clay Matrix to Ensure Uniform Dispersion in Drilling Fluids

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ABSTRACT

Zinc Oxide (ZnO) has received lot of attention as a nanostructured material because of unique properties rendering it suitable for various applications. One particular application focussed here for the first time is to form Clay-ZnO nanocomposites for use in drilling fluids to ensure uniform dispersion and superior rheology. Two major clays namely bentonite and attapulgite were tested. Bentonite is commonly used as a rheology modifier but faces the limitations of flocculation and instability at high temperature conditions. Attapulgite whereas, is a new clay material and have shown to be better than bentonite based clays. The rheology of drilling fluids plays an important role in controlling drilling operations. Severe drilling problems like lost circulation, pipe sticking, formation damage and high torque and drag are common in extended reach drilling operations that limits the performance and are mainly responsible for huge financial losses in the form of expensive drilling fluid additives and lost production time. This work presents an initiative to modify the commonly used clays by coating them with zinc oxide nanorods (sizes ranging from 6-10 nm) to maintain remarkable colloidal suspensions thus enabling homogeneous drilling fluid recipes.

Keywords: Zinc Oxide, Drilling Fluids, Attapulgite, Bentonite, Nanocomposite

1 INTRODUCTION

Recent developments in nanotechnology and the demonstration of various quantum size effects in nano-scale particles, implies that many novel devices of the future will be based on properties of nanomaterials [1]. Reports of zinc oxide (ZnO) nanostructures, especially nanowires, are of interest due to their potential applications in gas and chemical sensing [2], micro-lasers [3], field emitters [4], amongst others. Also reported for ZnO nanostructures (piezoelectric material) are applications as cantilevers, with size scales over 50–100 times smaller than the conventional cantilevers which show improved sensitivity and mechanical flexibility for applications in scanning probing microscopes [5]. A wide range of strategies have been explored by different groups for the synthesis of nanowires of ZnO [6–9].

Over the past decades, aluminosilicate clay minerals have attracted intense research activity because of their ability to form intercalation complexes with diverse guest species [10-12] There have been many reports on various intercalation compounds of the clay minerals containing organic molecules, metal complexes, metal oxides, and so on [13].

Apart from its marvelous breakthroughs in the field of electronics, in recent past ZnO has gained much attention as a potential material for synthesis of ZnO-Clay nanocomposites for various applications including agriculture, ceramics, paints and clays for water desalination.

An interesting application targetted here is to use ZnO-Clay nanocomposites for drilling fluids. The major hinderance in drilling fluids engineering is to have uiform dispersions of clays that limits the performance of the driling fluids thus calling the need for various additives to compensate for clay defficiencies. This incurs huge cost on overall drilling operation alongwith limited functionality [14-17].

ZnO due to its remarkable colloidal properties is expected to inpart stable coilloidal mechanisms to clays when combined. This work presents a detailed investigation on drilling fluids commonly used clays and their limitations. The work also highlight a technique to grow ZnO nanorods in clay matrix to endow the clays with superior colloidal suspensions while maintaining their original functionality. This will highly discourage flocculation of clays in water and thus render significant stability to the clays. Samples were prepared and two major clays bentonite and attapulgite were tested to form composites with ZnO nanorods.

2 BENTONITE (MONTMORILLONITE)

Bentonite consisting mainly of montmorillonite refers to a class of clay minerals scientifically known as smectite. Clay minerals are complex micro-crystals usually composed of aluminum silicate.

Detailed XRD analysis of bentonite powder was carried out and yields the following results.

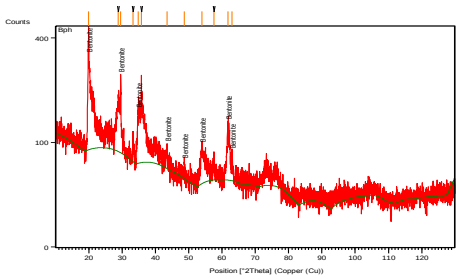

Figure – 1: XRD Analysis for chemical composition of Bentonite

The XRD peaks shown above (Figure 1) depicts that the tested bentonite powder contains mainly montmorillonite. Since it is well known from literature that Montmorillonite have high inter-particle forces and low inter-particle spacing and this is mainly responsible for the agglomeration of bentonite in water.

Another consequence of the presence of montmorillonite is the inconsistent hydraulic conductivity and the variable permeability of bentonite clay and the main reasons for which are identified to be the bentonite content (composition), dry unit weight, water content, type of bentonite and grain size distribution. This also limits the capability of bentonite to be used as a stable drilling fluid constituent.

Much of bentonite's usefulness in the drilling and geotechnical engineering industry comes from its unique rheological properties. Relatively small quantities of bentonite suspended in water form a viscous, shear thinning material. Most often, bentonite suspensions are also thixotropic, although rare cases of rheopectic behavior have also been reported. At high enough concentrations (~60 grams of -bentonite per liter of suspension), bentonite suspensions begin to take on the characteristics of a gel (a fluid with a minimum yield strength required to make it move). For these reasons it is a common component of drilling mud used to curtail drilling fluid invasion by its propensity for aiding in the formation of mud cake.

2.1 Limitations of Bentonite based drilling fluids:

Bentonite based drilling fluids have the limitation of flocculation and limited functionality at high pressure and pressure conditions. Because of high water absorption capability and swelling characteristics the dispersion behavior of bentonite is non uniform and have huge problem of flocculation which results in insufficient and inconsistent rheology of drilling fluids. Another main challenge is the instability of bentonite based drilling fluids at high temperatures and pressure conditions while extended reach drilling operations. Various additives have to be added to ensure uniform dispersion, maintaining appropriate rheology and for stability at HTHP conditions which incurs huge cost.

The SEM analysis showed that commercially available bentonite for drilling fluids have a spherical structure. Figure 2 shows the SEM image of bentonite based drilling fluid and agglomeration is clearly seen.

Figure – 2: SEM image of Bentonite (agglomerated)

The sticking of the particles is obvious and this is mainly responsible for inconsistent performance of bentonite based drilling fluids.

3 ATTAPULGITE (PALYGORSKITE)

Attapulgite is a kind of crystalloid hydrous magnesium-aluminum silicate mineral, having a special laminated chain structure in which there is a crystalline lattice displacement existed. Thus it makes the crystals contain uncertain quantities of Na+, Ca+, Fe3+ and Al, and present in the shape of needles, fibers or fibrous clusters as shown in figure 3. Attapulgite has very good colloidal properties such as: specific features in dispersion, high temperature endurance, salt and alkali resistance, and also high adsorbing and de-coloring capabilities. Furthermore, attapulgite has certain plastic and adhesive characters. Attapulgite clays are a composite of smectite and palygorskite. Smectite are expanding lattice clays of which bentonite is a commonly known generic name for smectite clays. The palygorskite component is an acicular bristle-like crystalline form which does not swell or expand.

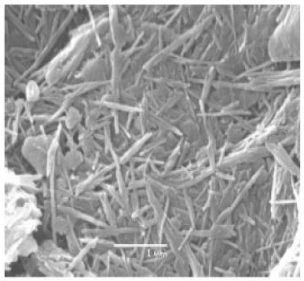

Figure – 3: SEM image of Regular Attapulgite (needle like clusters)

3.1 Advantages over Bentonite:

Palygorskite (major constituent of attapulgite) is a kind of natural hydrous clay mineral with fibrous rod-like microstructure. The special nanorods structure and large

specific surface area can endow palygorskite with many unique physical and chemical properties; therefore, palygorskite attracted the interest to be used as efficient and stable rheology modifier for drilling fluids. Besides drilling fluids, as an inexpensive natural mineral, palygorskite has been applied in many areas such as inorganic–organic polymer hybrids, nanofiller, fertilizer suspension, drilling fluids, oil refining, pharmaceutical industries, catalyst, catalyst support, etc. Huge reserves of attapulgite are available in the Sultanate of Oman.

Figure 4 shows the SEM image of raw attapulgite in which the needles intermingled and flocculated with each other can be seen clearly.

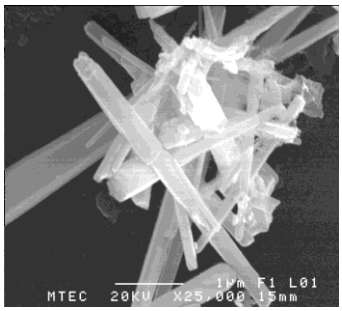

Figure – 4: SEM image of Regular Attapulgite (flocculated and intermingled)

Even though the needle like morphology provides a higher surface area than the spherical morphology of bentonite but the intermingling and flocculation limits the maximum exposure of attapulgite particles with the solvent (i.e. water in water based muds). It is thus an issue of utmost importance to disperse the particles in the solvent to the maximum extent by breaking the clusters and unfolding the chains to maximize the exposure area.

Detailed XRD analysis of raw attapulgite powder was carried out and yields the following results.

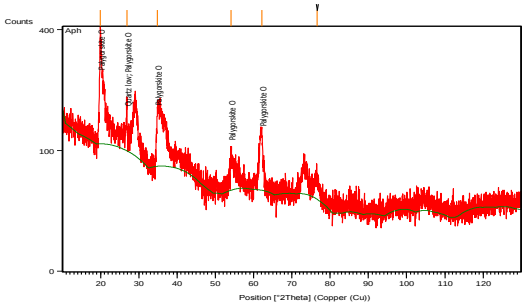

Figure – 5: XRD Analysis for chemical composition of Attapulgite – Source: SQU

The XRD peaks (Figure 5) show that the tested Attapulgite powder contains mainly palygorskite

Due to this presence of palygorskite Attapulgite forms gel structures in fresh and salt water by establishing a lattice structure of particles connected through hydrogen bonds. Attapulgite, unlike bentonite, will form gel structures in salt water and is used in special salt water drilling mud for drilling formations contaminated with salt. Palygorskite particles can be considered as charged particles with zones of + and - charges. It is the bonding of these alternating charges that allow them to form gel suspensions in salt and fresh water.

4 FORMING CLAY-ZnO COMPOSITE

4 mM solution of Zinc acetate was prepared by dissolving 0.035 gm of zinc acetate in 40 ml of ethanol to have the stock solution A. The solution was prepared at 50 ^{O} C under rigorous stirring for 2 hours. After obtaining a clear solution it was allowed to cool down to room temperature. 2 mM solution of NaOH was prepared by dissolving 0.0032 gm of NaOH in 40 ml ethanol to have stock solution B. The solution was also stirred rigorously for 2 hours at 50 ^{O} C. Later was allowed to cool to room temperature. 1 mM solution of Attapulgite clay was prepared by dissolving 0.04 gm of Attapulgite in 50 ml ethanol. The solution was sonicated in pre heated water bath for 1 hour at 30 ^{O} C. This is stock solution C. Stock solution A (20 ml) and C (20 ml) were mixed together and rigorously stirred for 30 minutes at 70 ^{O} C, to form solution D. After cooled to room temperature the solution D was then slowly added by 20 ml of solution B under continuous stirring. This formed solution E. Solution E was then cover, and was put in a pre heated water bath at 60 ^{O} C for 2 hours for hydrolysis. The samples were then characterized by SEM.

5 OBSERVATIONS AFTER CHARACTERIZATION

5.1 ZnO-Bentonite Nano-Composite

Bentonite samples were taken for characterization by scanning electron microscope as show in figure 2 which revealed that bentonite basic structure is flake like. The particles are held in the form of big chunks. To determine the particle size TEM analysis was carried out on the same bentonite sample as show in figure 6.

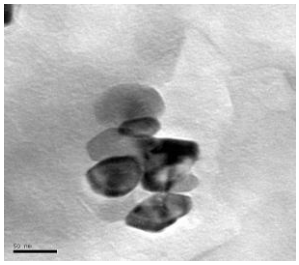

Figure – 6: TEM image of Bentonite (agglomerated)

From the TEM analysis it was found that the particle size distribution is in the range of 50 nm but again flocculation is clearly visible. In order to engulf this problem of flocculation to ensure uniform dispersion the

bentonite clay was processed as explained in section 4. The growth of ZnO nanorods in bentonite clay matrix resulted in uniform seeding patterns as shown in figure 7.

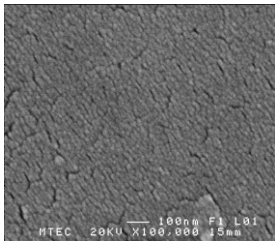

Figure – 7: SEM image of ZnO-Bentonite Nanocomposite

It is very obvious that the ZnO nanoparticles are well adapted by the bentonite clay matrix and are uniformly dispersed that is the main objective of this application to be used in drilling fluids. The particle size distribution is very small i.e. in the range of 7-10 nm and are uniformly dispersed.

5.2 ZnO-Attapulgite Nano-Composite

The needle like raw attapulgite as shown in figure 3 and 4 was also treated through the same process as explain in section 4. As of bentonite, attapulgite also was found to well adapt the ZnO nanorods in its matrix. The SEM results of ZnO-Attapulgite nanocomposite are shown in figure 8.

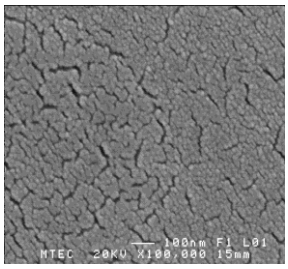

Figure – 8: SEM image of ZnO-Attapulgite Nanocomposite

The SEM results showed similar results for attapulgite as of bentonite. A mush smaller particle size distribution and uniform dispersion was assured.

6 CONCLUSION

Detailed investigation was carried out on common drilling fluid additive bentonite and a new potential material attapulgite. The SEM and XRD analysis reveled that bentonite have a spherical structure and the particles are agglomerated. This limits the funcionality of bentonite based drilling fluids to offer consistent performance. Attapulgite on the other hand posses needle like structure that are intermingled with each other. Attapulgite based drilling fluids offers better rheological properties than bentonite based drilling fluids due to different morphologies and chemical composition. The attempt of forming ZnO-clay nanocomposites was found useful in that the particle size distribution was significantly small and a uniform seeding pattern was observed. Both attapulgite and bentonite was found to adapt well with ZnO nanoparticles and a firm bonding was noticed. This helps in getting uniform and stable clay suspensions in drililng fluids. Various concentrations of clay and ZnO nanoparticles can be tested to modify the rheology of drilling fluids.

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